

Brominated flame retardant polymers: a possible source for emerging brominated aromatic compounds in the environment.

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Supporting Information

Additional information to complete the “Material and methods” section is described. Chemical structure of PBS-64, BC-58, and FR-1025 are presented in Figure S1. Figure S2 depicts the schematic diagram of the sampling system used for the thermal experiments. Figure S3 shows ECNI GC/MS chromatograms obtained after thermal stress experiments on PBS-64 at room temperature and under increasing temperature. Figures S4 to S15 show full-scan EI mass spectra obtained for brominated compounds released from polymeric BFRs. Figure S16 shows ECNI GC/MS chromatograms obtained after thermal stress experiments on PBS-64 at room temperature and increasing temperature up to 100 °C. Figure S17 shows the ECNI GC/MS chromatograms obtained for an air sample. Table S1 lists some physico-chemical properties of PBTo, PBEB, HBB and the North America and coastal waters area used to run the Level III fugacity model. Table S2 lists the chemical structures of brominated compounds released from polymeric BFRs.

Thermal experiments

GC and MS operating conditions for thermal experiments:

The GC operating conditions, with helium as carrier gas, were as follows: injector port at 280 °C, GC oven at 90 °C for 1.5 min, then to 240 °C at 20 °C min⁻¹, then to 310 °C at 8 °C min⁻¹, and hold for 5 min. MS detector was operated in electron capture negative ion (ECNI) mode at an ion source temperature of 175 °C and an ion source pressure of 1.0 torr using methane as reagent gas. Selected ions m/z 79 and 81 were monitored to identify brominated compounds released during thermal experiments. Electron impact (EI) ionization mode measurements were made at 70 eV and 175 °C ion source temperature.

Environmental measurements

Treatment of environmental samples:

PUF samples were Soxhlet extracted in petroleum ether (PE) overnight. α -d6-HCH and Mirex were added as surrogates to monitor recoveries. Then, extracts were eluted with about 12 mL DCM/PE (10:90 v/v) on a 2 g neutral deactivated alumina (6% water) column. Finally, extracts were transferred to isooctane and concentrated to about 300 μ L prior to GC-MS analysis. Internal standard used was 13C12 PCB-105.

GC and high resolution MS operating conditions:

The GC injection port was configured for split/splitless injection at a temperature of 280°C. The GC column was maintained at 100°C for 3 minutes, and then ramped at 5°C/min to 320°C. Helium was used as the carrier gas in constant pressure mode. Sample ionization was performed by electron ionization (EI) at an electron voltage ranging from 30 to 40eV depending on the optimization

44 parameters of the instrument. Source temperature was 280°C and the resolving power of the
45 analyzer was at least 10,000. The mass spectrometer was operated in SIM mode to monitor the two
46 most abundant isotopic ions of the most abundant fragment or molecular ion clusters observed in the
47 full mass spectra of PBTo, PBEB, and HBB. PBTo was identified by monitoring isotopic ions m/z
48 485.6111 and 487.6090 from the molecular ion. PBEB was identified by monitoring isotopic ions
49 m/z 484.6032 and 486.6012 of the fragment resulting from the loss of a methyl group by the
50 molecular ion. HBB was identified by monitoring isotopic ions m/z 547.5078 and 549.5058 from the
51 molecular ions. Isotopic ions m/z 483.7131 and 485.7111 were monitored for PBDE-47.

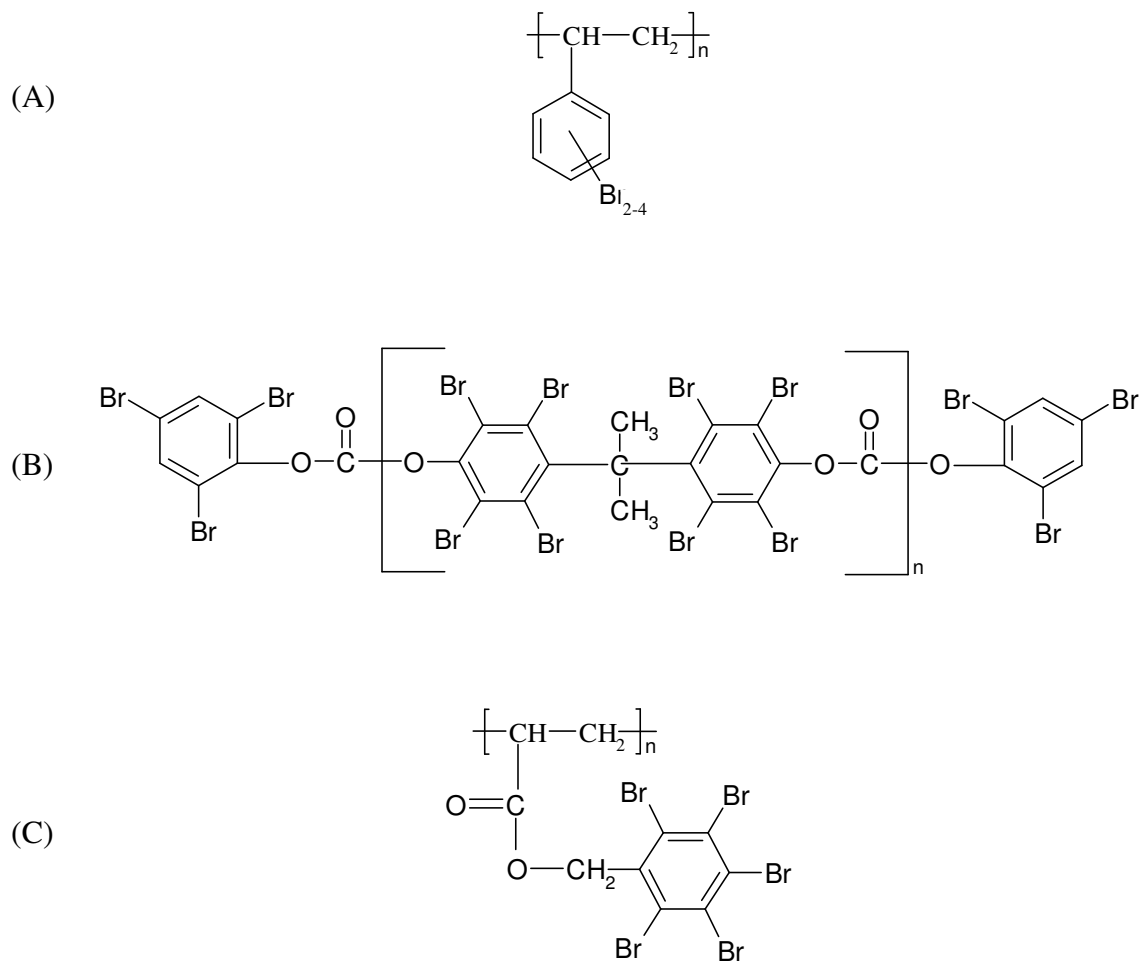


Figure S1: Chemical structure of (A) PBS-64, (B) BC-58, and (C) FR-1025 polymers.

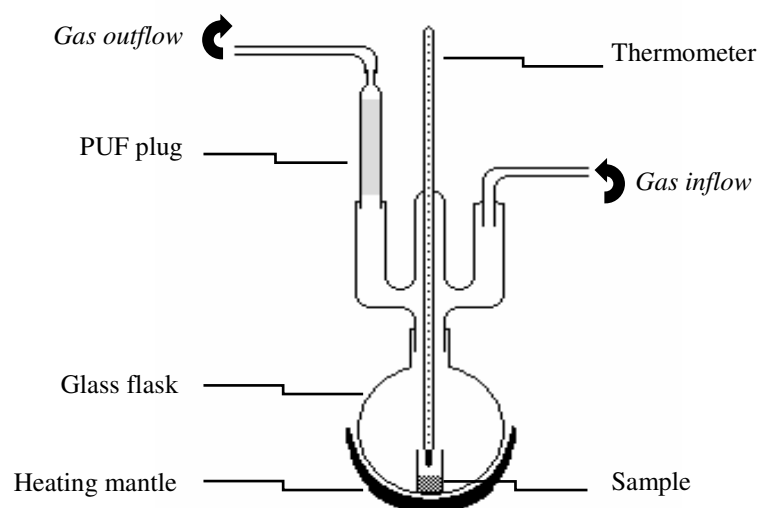


Figure S2: Schematic diagram of the sampling system adapted from (19).

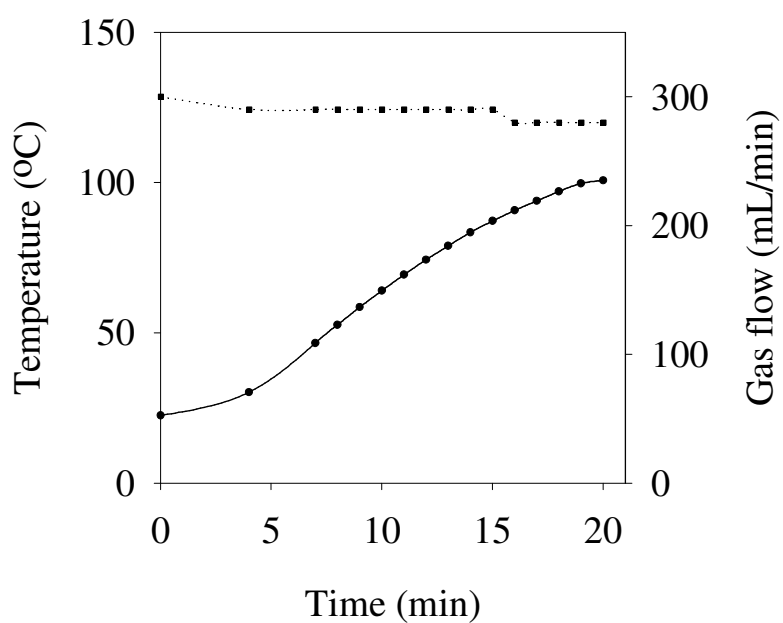


Figure S3: Temperature and gas flow vs time profiles used for the heating of PBS-64, BC-58, and FR-1025 from room temperature to 100 °C.

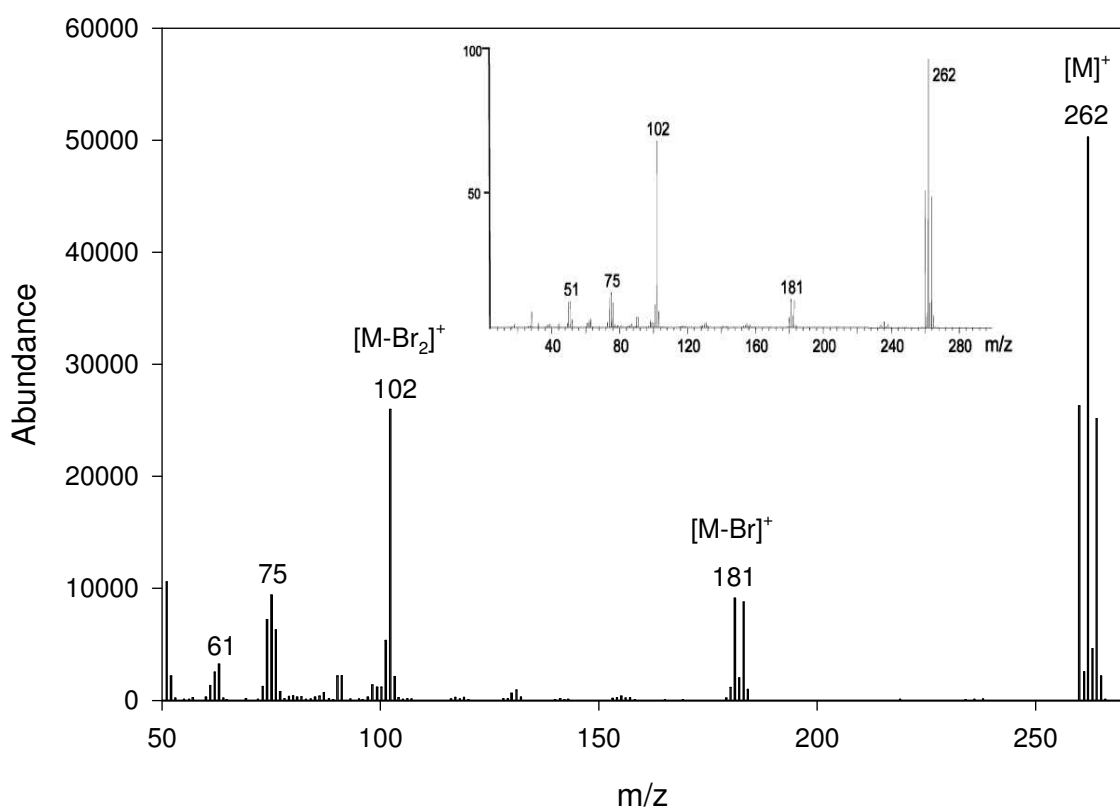


Figure S4. Full-scan EI mass spectra obtained for dibromostyrene isomers (compounds (1), (2), and (3) in Figure 2A). Insert shows reference full-scan EI mass spectrum from (23). See Table S2 for chemical structure.

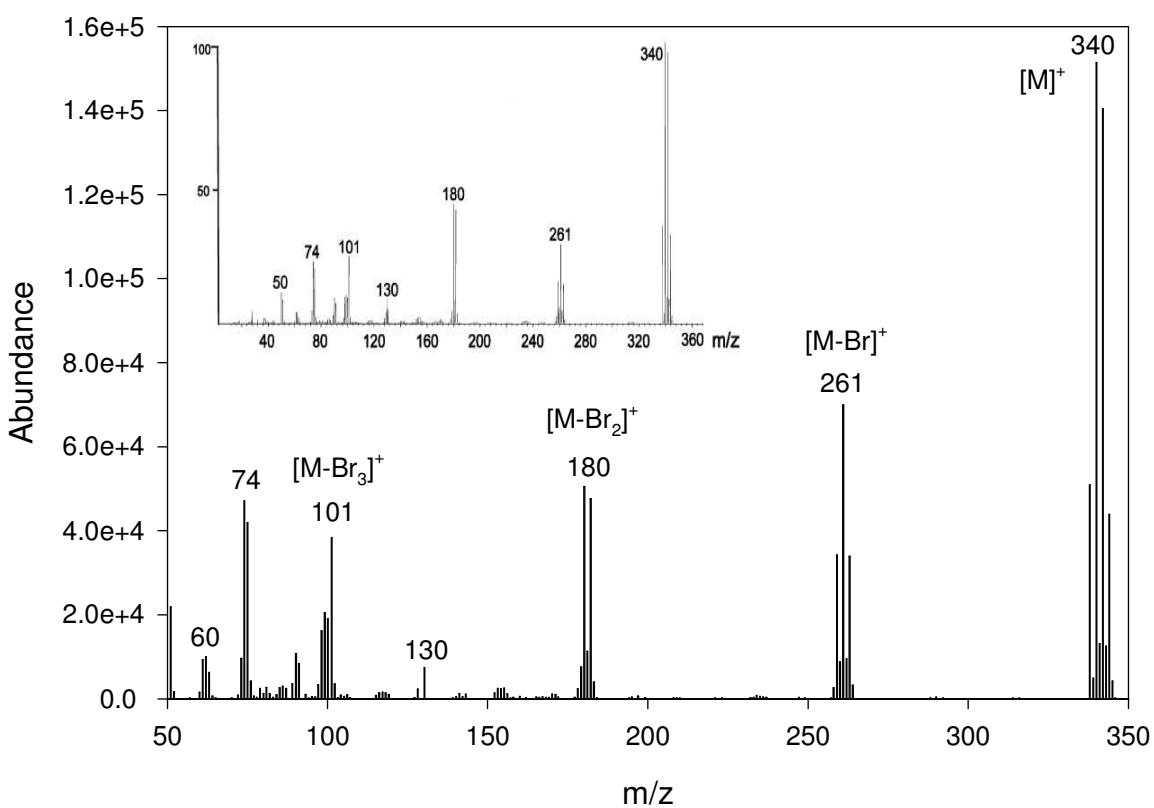


Figure S5: Full-scan EI mass spectra obtained for tribromostyrene isomers (compounds (4), (5), and (6) in Figure 2A). Insert shows reference full-scan EI mass spectrum from (23). See Table S2 for chemical structure.

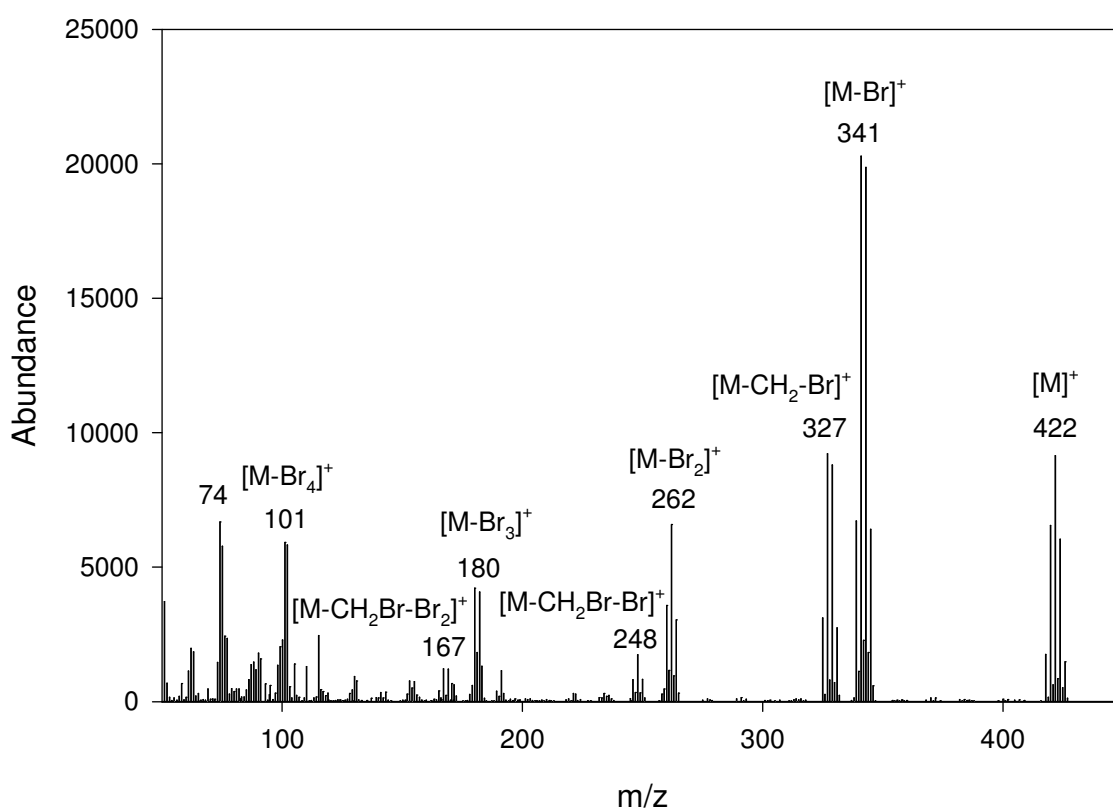


Figure S6. Full-scan EI mass spectrum obtained for the (bromoethenyl)-tribromobenzene isomer (compound (7) in Figure 2A). See Table S2 for chemical structure.

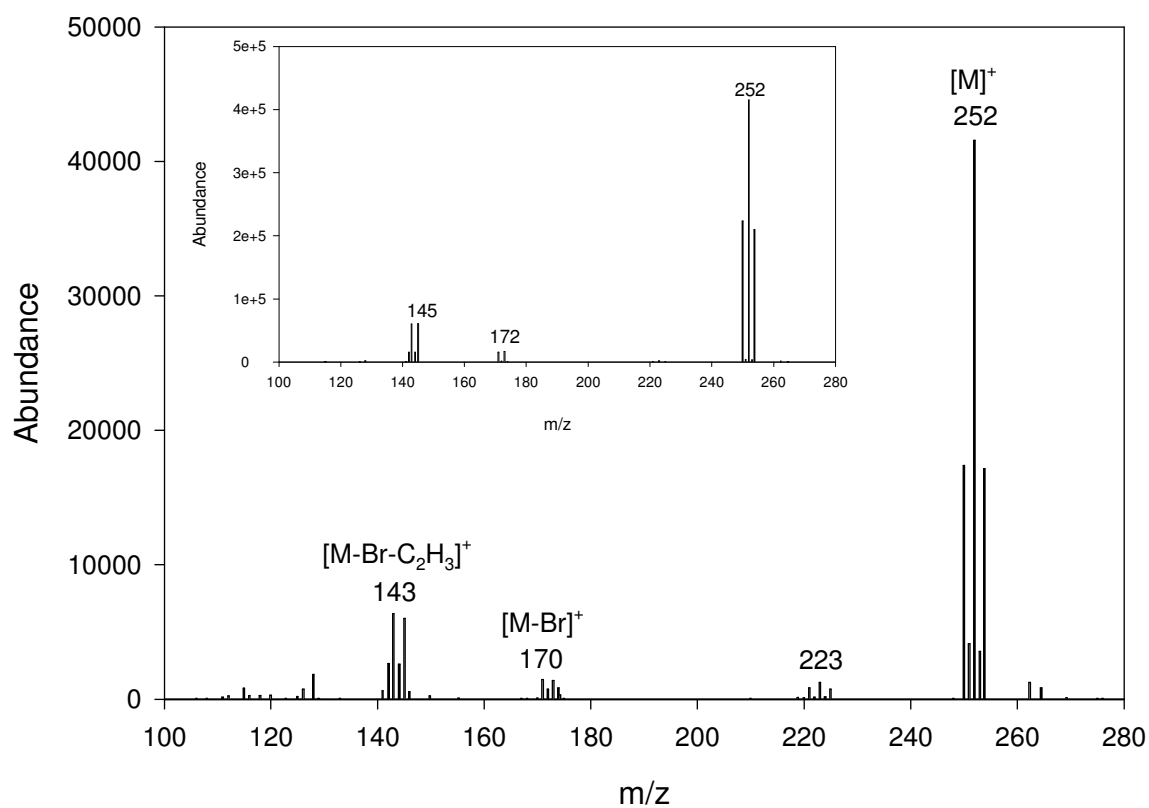


Figure S7: Full-scan EI mass spectrum obtained for the dibromophenol isomer (compound (8) in Figures 2B and 2C). Insert shows reference full-scan EI mass spectrum obtained from authentic material. See Table S2 for chemical structure.

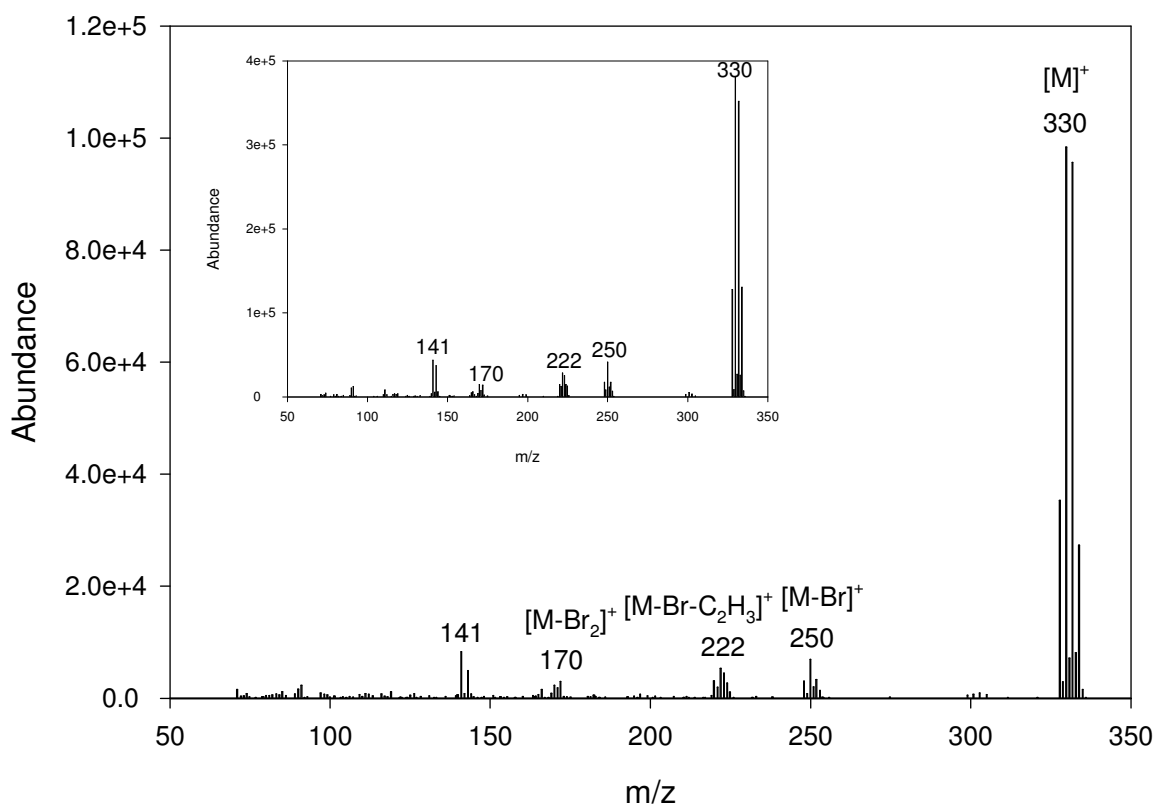


Figure S8: Full-scan EI mass spectrum obtained for the tribromophenol isomer (compound (9) in Figures 2B and 2C). Insert shows reference full-scan EI mass spectrum obtained from authentic material. See Table S2 for chemical structure.

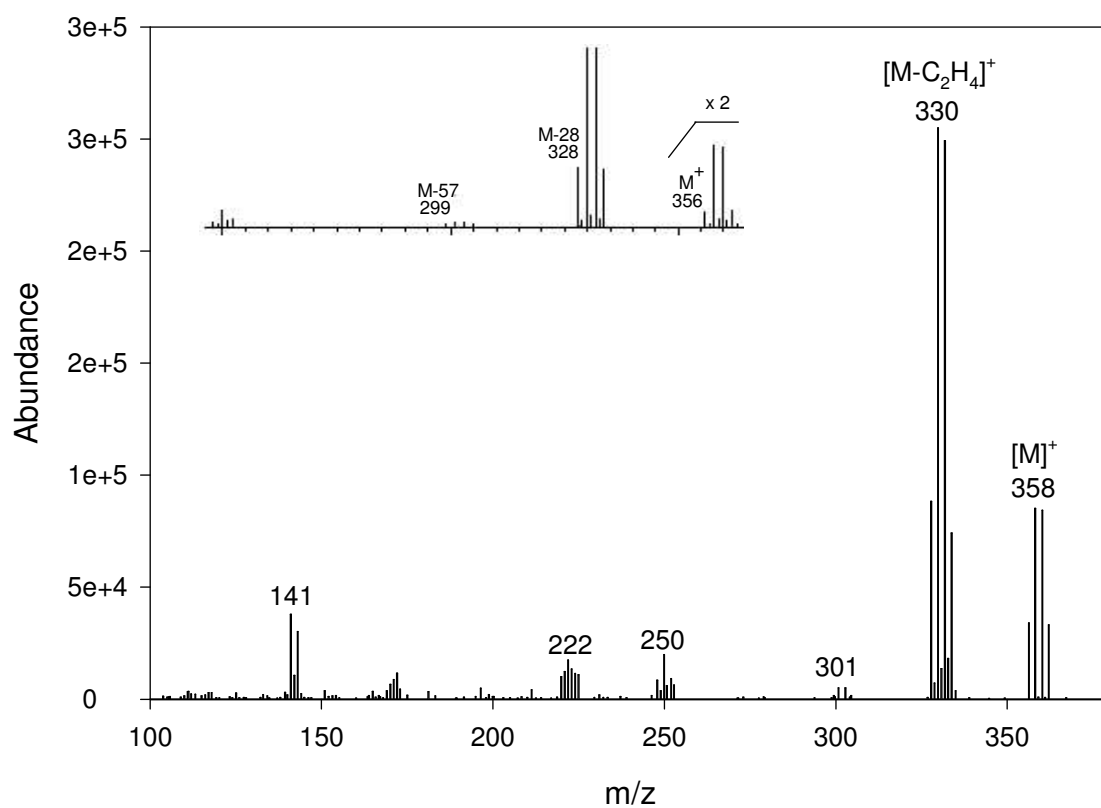


Figure S9: Full-scan EI mass spectrum obtained for the tribromophenetole isomer (compound (10) in Figures 2B and 2C). Insert shows reference full-scan EI mass spectrum reported from (24). See Table S2 for chemical structure.

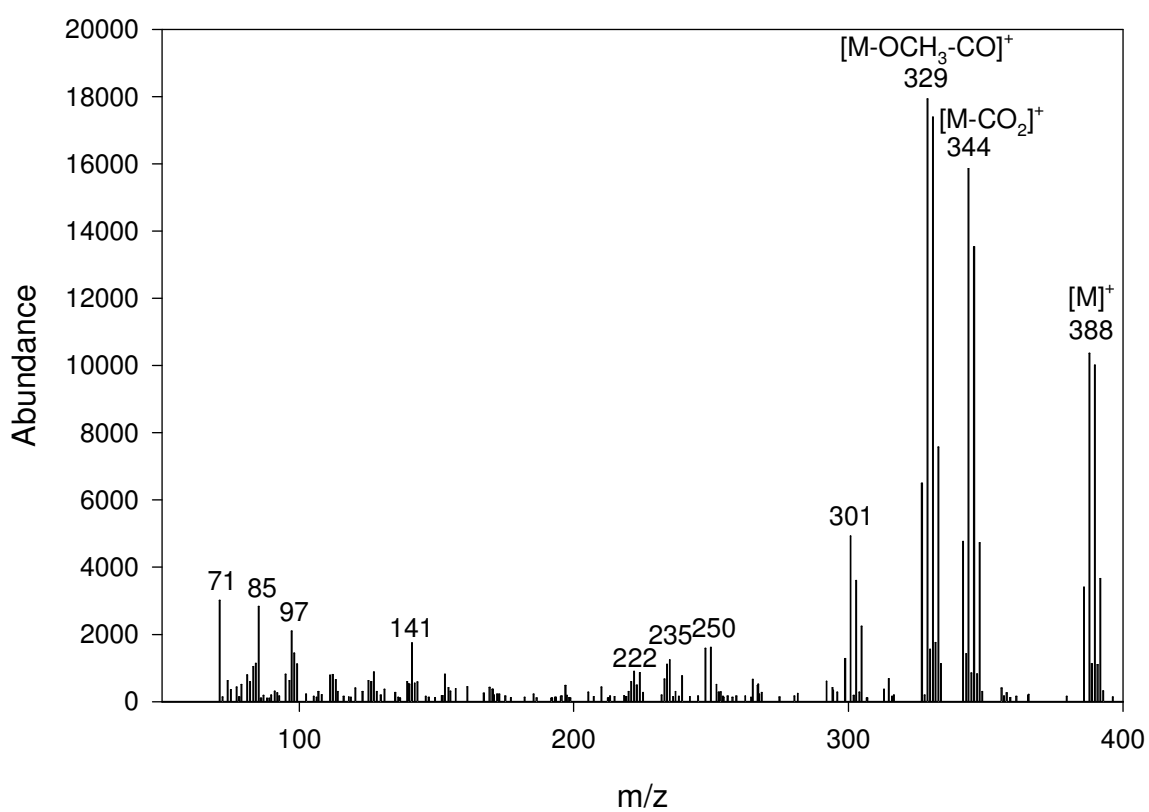


Figure S10: Full-scan EI mass spectrum obtained for the tribromophenyl methyl carbonate isomer (compound (11) in Figures 2B and 2C). See Table S2 for chemical structure.

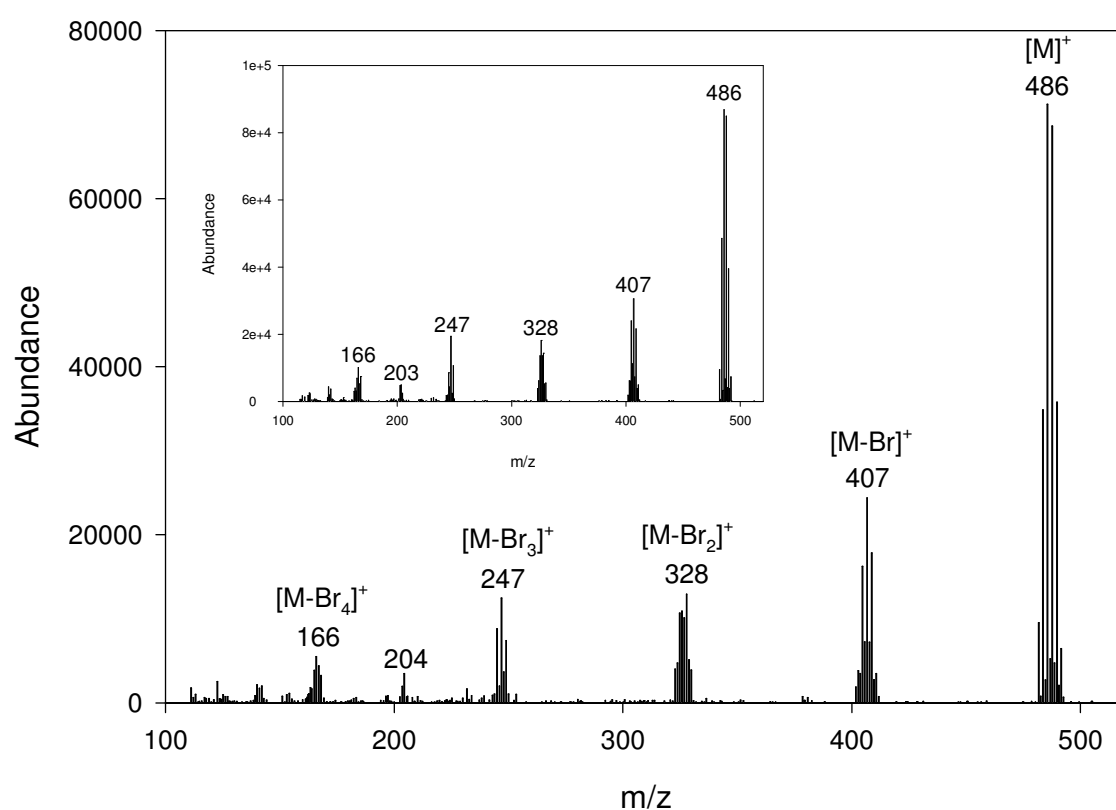


Figure S11: Full-scan EI mass spectrum obtained for 2,3,4,5,6-pentabromotoluene (compound (12) in Figures 2B and 2C). Insert shows reference full-scan EI mass spectrum obtained from authentic material. See Table S2 for chemical structure.

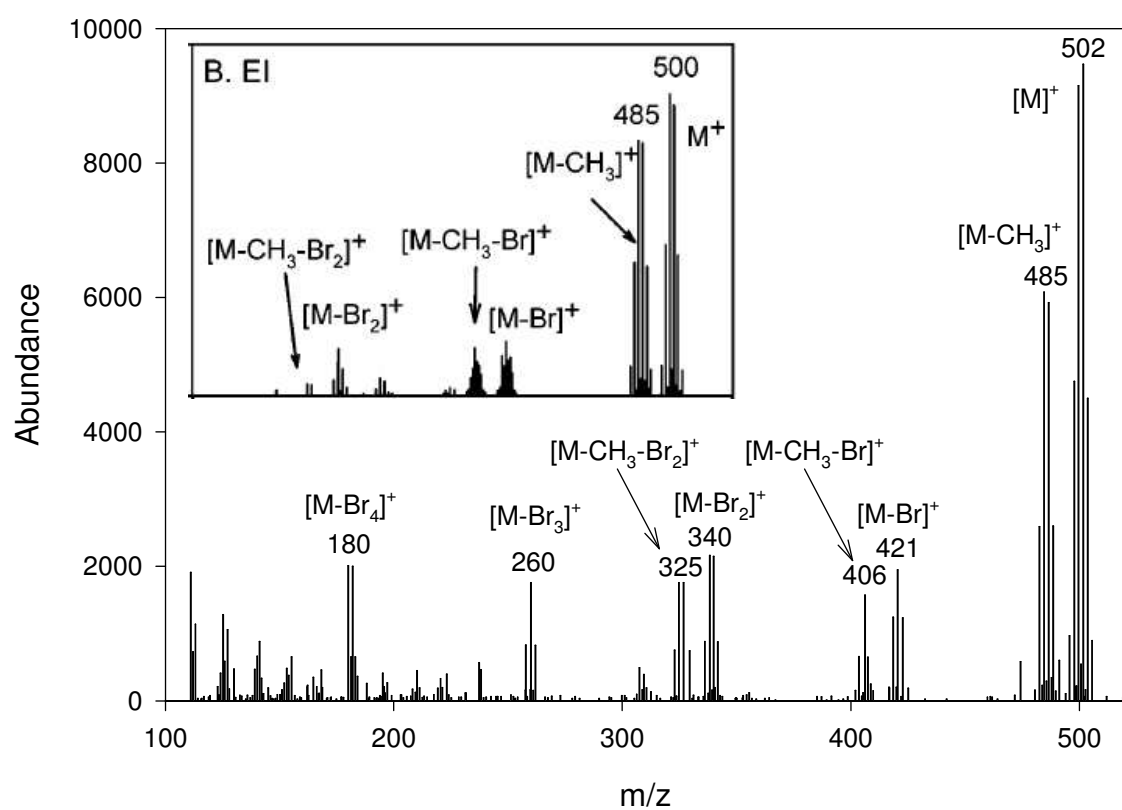


Figure S12: Full-scan EI mass spectrum obtained for 2,3,4,5,6-pentabromoethylbenzene (compound (13) in Figures 2B and 2C). Insert shows reference full-scan EI mass spectrum from (25). See Table S2 for chemical structure.

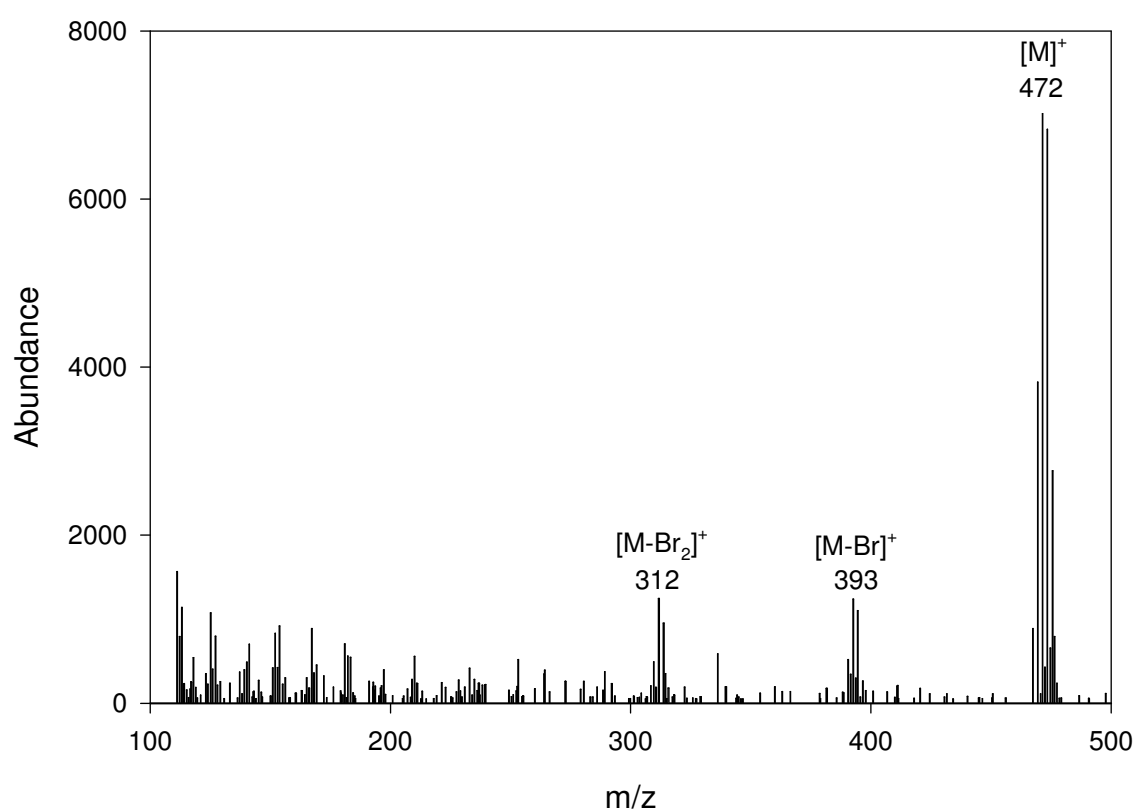


Figure S13: Full-scan EI mass spectrum obtained for 1,2,3,4,5-pentabromobenzene (compound (14) in Figure 2C). See Table S2 for chemical structure.

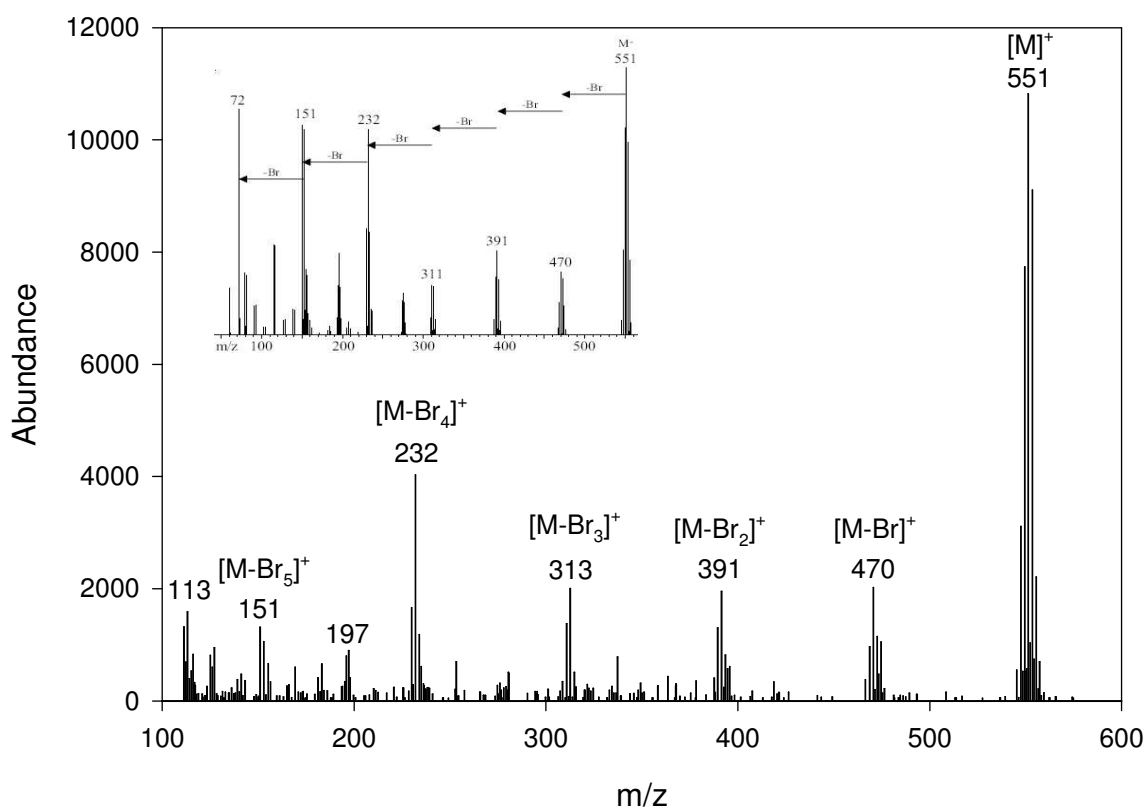


Figure S14: Full-scan EI mass spectrum obtained for hexabromobenzene (compound (15) in Figure 2C). Insert shows reference full-scan EI mass spectrum from (26). See Table S2 for chemical structure.

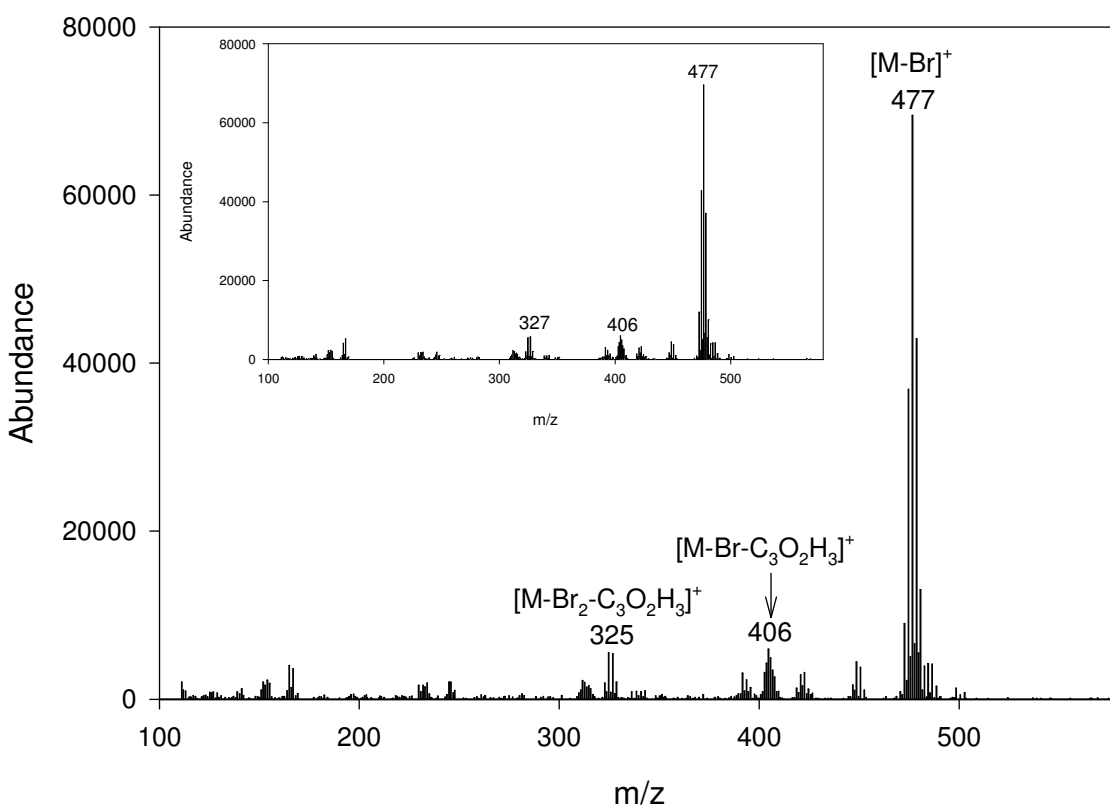


Figure S15: Full-scan EI mass spectrum obtained for pentabromobenzyl acrylate (compound (16) in Figure 2C). Insert shows reference full-scan EI mass spectrum obtained from authentic material. See Table S2 for chemical structure.

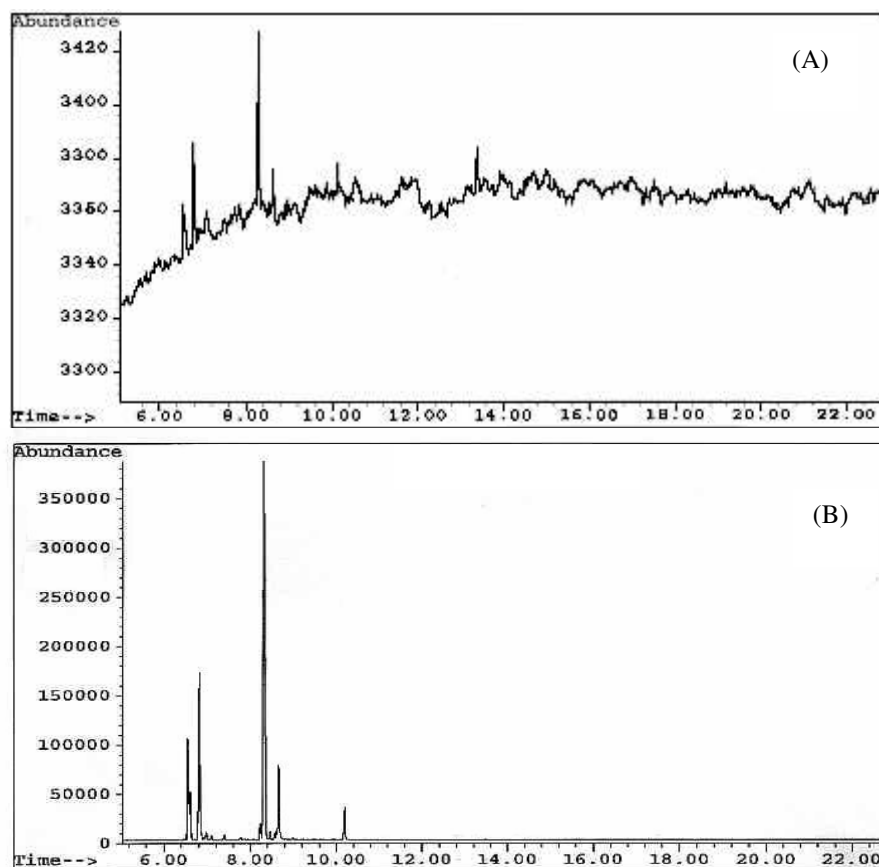


Figure S16: ECNI GC/MS chromatograms obtained after thermal stress experiments on PBS-64 at
A) room temperature and B) increasing temperature up to 100 °C.

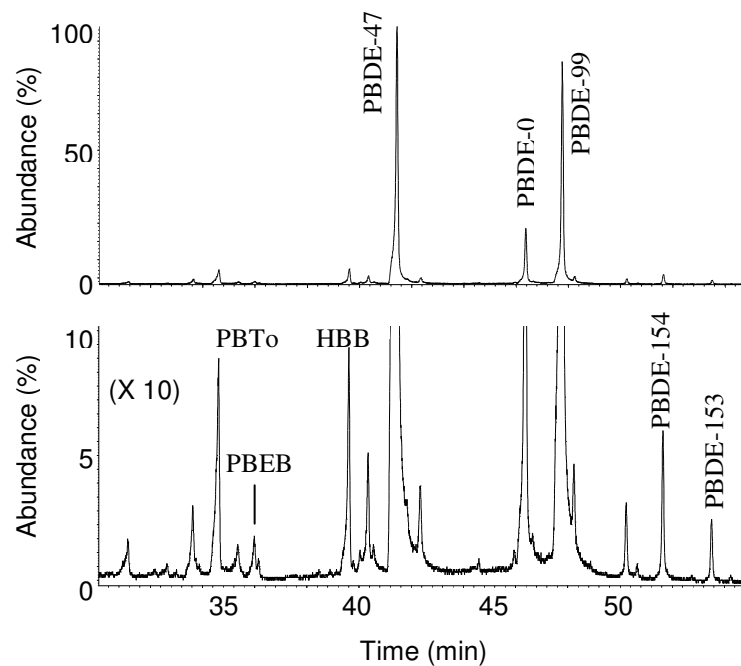



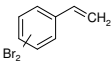

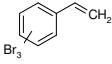
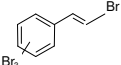
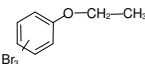
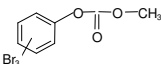


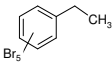

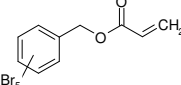
Figure S17. ECNI GC/MS chromatograms (m/z 79+81) obtained for an air sample collected at Egbert. Zoom in (X10) is also shown.

Table S1: Molecular weight, melting point, and estimated water solubility, vapor pressure, and half-lives in different environmental media of volatile brominated compounds of interest. Dimensions of the area of North America and coastal waters used to run the Level III fugacity model are also shown. Default values were used for other environmental properties of the Level III fugacity model.

Compound	MW ^a (g/mol)	MP ^b (°C)	WS ^{c,j} (g/m ³)	VP ^{d,j} (Pa)	Log K _{ow} ^{e,j}	t _{1/2} air ^{f,j} (d)	t _{1/2} water ^{g,i} (d)	t _{1/2} soil ^{h,j} (d)	t _{1/2} sed ^{i,j} (d)	Air depth (m)	Air area (m ²)	Water area (m ²)
PBTo	487	288	9.35 10 ⁻⁴	1.95 10 ⁻⁵	7.0	88	180	360	1 600	10 000	5.30 10 ¹³	2.87 10 ¹³
PBEB	501	138	2.90 10 ⁻⁴	6.20 10 ⁻⁴	7.5	14	180	360	1 600	10 000	5.30 10 ¹³	2.87 10 ¹³
HBB	552	326	1.60 10 ⁻⁴	2.24 10 ⁻⁶	6.1 ^k	1 400	180	360	1 600	10 000	5.30 10 ¹³	2.87 10 ¹³

^a MW = molecular weight; ^b MP = melting point; ^c WS= water solubility; ^d VP = vapor pressure; ^e K_{ow} = octanol-water partition coefficient; ^f t_{1/2}air = atmospheric half-life; ^g t_{1/2}wat. = water half-life; ^h t_{1/2}soil = soil half-life; ⁱ t_{1/2}sed. = sediment half-life; ^j WS, VP, Log K_{ow}, t_{1/2}air, t_{1/2}wat., t_{1/2}soil, t_{1/2}sed. were estimated using the quantitative structure property estimation Program EPI SuiteTM (19) or PBT profiler (20); ^k experimental data from (38);

450 Table S2: Structures of volatile brominated organic compounds released by polymeric BFRs

Compound	Structure	Polymeric BFR	Peak ^a
Dibromophenol		BC-58 FR-1025	(8)
Dibromostyrenes		PBS-64	(1), (2), (3)
Tribromophenol		BC-58 FR-1025	(9)
Tribromostyrenes		PBS-64	(4), (5), (6)
(bromoethenyl)-tribromobenzene		PBS-64	(7)
Tribromophenetole		BC-58 FR-1025	(10)
Tribromophenyl methyl carbonate		BC-58 FR-1025	(11)
Pentabromobenzene		FR-1025	(14)
Pentabromotoluene		BC-58 FR-1025	(12)
Pentabromoethyl benzene		BC-58 FR-1025	(13)
Hexabromobenzene		FR-1025	(15)
Pentabromobenzyl acrylate		FR-1025	(16)

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452 ^a Peak refers to the numbering used in Figure (1)

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